Dkt. 45888-1

IN THE UNITED STATES
PATENT AND TRADEMARK OFFICE

| | |
|---|---|
| Application No. | : 09/895,334 |
| Applicant | : Rejean AUBE |
| Filed | : July 2, 2001 |
| Title | : DELAY COMPOSITIONS AND DETONATION DELAY DEVICES UTILIZING SAME |
| Art Unit | : 3641 |
| Examiner | : Aileen Baker Felton |

**DECLARATION UNDER 37 C.F.R. §1.132**

I, Rejean AUBE, declare that:

1. I am the sole applicant named in the above-identified application, and am the sole inventor of the invention described and claimed therein.

2. Attached as EXHIBIT 1 hereto is a copy of an internal Experimental Test Report of Orica Canada (an affiliate of the assignee of the above-identified application) designated ETR #1R-86-141 and dated November 2000, describing tests performed by me and/or under my direction on delay compositions of $BaSO_4$ and silicon (referred to therein as "Y composition") with additions of 3, 5, 7 and 9% red lead. The effect of the red lead additions on delay timing is shown in the graph on page 6 of EXHIBIT 1, reproduced as FIG. 3 of the above-identified application. The effect of these red lead additions on the coefficient of variation (C.V.) is shown in the graph on page 7 of EXHIBIT 1, reproduced as FIG. 4 of the above-identified application. The two graphs on page 8 of EXHIBIT 1 are respectively reproduced as FIGS. 5 and 6 of the above-identified application. The graph on page 9 of EXHIBIT 1 is reproduced as FIG. 7 of the

above identified application, and that on page 10 of EXHIBIT 1 is reproduced as FIG. 8 of the above-identified application.

3. Attached as EXHIBIT 2 hereto is a copy of a internal Experimental Test Report of Orica Canada designated ETR #1R-86-142 and dated December 2000, describing further tests performed by me and/or under my direction on delay compositions of $BaSO_4$ and silicon modified by additions of 9 to 20% red lead. The effect of the red lead additions on delay timing is shown in the upper graph on page 5 of EXHIBIT 2, reproduced (with an inadvertent error in the delay timing value for 5% red lead) as FIG. 9 of the above-identified application. The effect of these red lead additions on the coefficient of variation (C.V.) is shown in the lower graph on page 5 of EXHIBIT 2, reproduced as FIG. 10 of the above-identified application.

4. The tests reported in EXHIBIT 1 constituted my first evaluation of small additions of red lead into "Y composition" and these additions extended only up to 9% red lead. The tests reported in EXHIBIT 2 constituted a continuation of small incremental additions of red lead to the same master batch of "Y composition," beginning at 9% and extending up to 20%. The graph at page 5 of EXHIBIT 2 (corresponding to FIG. 9 of the above-identified application) combines the whole set of data from the two sets of tests, with the delay timing values for additions of 3, 5 and 7% red lead copied from EXHIBIT 1 (the test set of EXHIBIT 2 started with an addition of 9% red lead, and I used the delay timing value of 2725 ms measured for 9% red lead in that second set of tests in the last-mentioned graph and FIG. 9).

5. Recently, in reviewing the drawings of the above-identified application, I have noted that the delay timing value for 5% red lead in FIG. 9 is erroneously given as 2766 ms. The correct value, as set forth in FIG. 3 and in the upper graph on page 5 of EXHIBIT 2 (from which FIG. 9 was copied), is 2756 ms.

6. In the range of delay timing between 2500 and 3000 ms, a typical standard deviation up to 100 ms is to be expected as normal, within the same group of detonations fired.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United Stares Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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ETR # 1R-86-141

DATE: November 2000.

Cc: Geoff Anderson, Ross Gourlay, Ron Stewart, Jim Simon, Art Bowman, Jean-Luc Arpin, Bob Greenhorn, Réjean Aubé, Brownsburg files (2).

# EXPERIMENTAL TEST REPORT

| | | | |
|---|---|---|---|
| **Product**: | DNES detonators | **Instituted by**: | R.F. Stewart |
| **Component**: | Composition Y in zinc elements | **Dept.**: | Technology |
| **Operation**: | Product evaluation | | |
| **Date Started**: | September 2000 | **Date Finished**: | November 2000 |

## SUBJECT

Development of a reliable LP delay composition for the rigid zinc element technology.

## OBJECTIVE

Assess functioning, delay timing and robustness of propagation of detonators assemblies having a main zinc rigid element filled with the $BaSO_4$/Si system + small addition of $Pb_3O_4$ in the composition.

## CONCLUSION

1) It appeared that an addition between 4% to 7% of Hammond Red Lead in composition Y and loaded in rigid zinc elements at a density between 1.80g/cc to 2.00g/cc produced a very good timing accuracy and functioned reliably at –40°C in either ORICA or DNES detonator shell design.

## RECOMMENDATION

1) Assess the effect on detonator performances, of adding a water soluble binding agent to improve the flow properties of compositions G, E and modified Y.

R. Aubé______________

Approved by______________

# INDEX

## 1.0 Background

The DNES manufacture acquisition is leading to the development of an hybrid detonator where both technologies are combined to supply an improved non-electric initiating system for the European market. The evaluation of the DNES units (ETR1R-86-138) and the modifications done on the detonator construction (ETR1R-86-140) have highlighted that the gassy delay mixture used in LP's is not compatible with the use of a sealer element. The use of a sealer element was found to improve the timing stability under various shock tube configuration (straight assembly "vs" TRB) for other "less gassy" compositions.

Based on previous testing, the Y composition presently used by ORICA in drawn lead elements will not function reliably in rigid elements. The use of this composition in rigid elements will therefore require some changes to the composition itself.

## 2.0 Introduction

The work done by Beck at Ardeer in 1992 about the mechanism of combustion of the $BaSO_4/Si$ system showed that Y composition could be used in rigid element if an appropriate flux is added to the mixture in order to reduces its melting point and then facilitate the powder ignition and, robustness to combustion.

The use of a flux in composition "Y" was also assessed by the author in 1997 during the shock stop program (ETR 1R-86-115) and showed that the presence of 5% red lead reduced the melting point of "Y" comp and produced a more accurate delay timing in drawn lead. Although it was not considered to be a solution to reduce the shock-stop phenomenon, the presence of red lead in Y has the advantage of being a well known ingredient without any compatibility concern and also, shock stop is not considered as an issue with the rigid element technology but it will be evaluated when the final formulation containing an appropriate binding agent being determined.

## 3.0 Powder mixing

**3.1 DRY MIX**: A production mix sample of Y comp. lot 1952 was first divided in 5 small mixes of 10 gm in small velostat container. The first sample was left intact as a reference control sample while an addition of 3%, 5%, 7%, and 9% of Red Lead was made in the subsequent mixes. Conductive rubber balls were added to the mixes to help ingredients mixing together during tumbling of velostat containers.

**3.2 WET MIX**: A 1Kg batch of a modified Y composition having 6 % Red Lead in it was prepared in lab. 72. The respective mass ratios for the ingredients were 51.7% of $BaSO_4$ ,(0.8m$^2$/gm surface area) 42.3% for the Silicon (12 hours milled) and 6% of Hammond $Pb_3O_4$. Athough the Red Lead was added at first in the medium to ensure a good dispersion of particles, the regular wet mixing process for Y composition was followed.

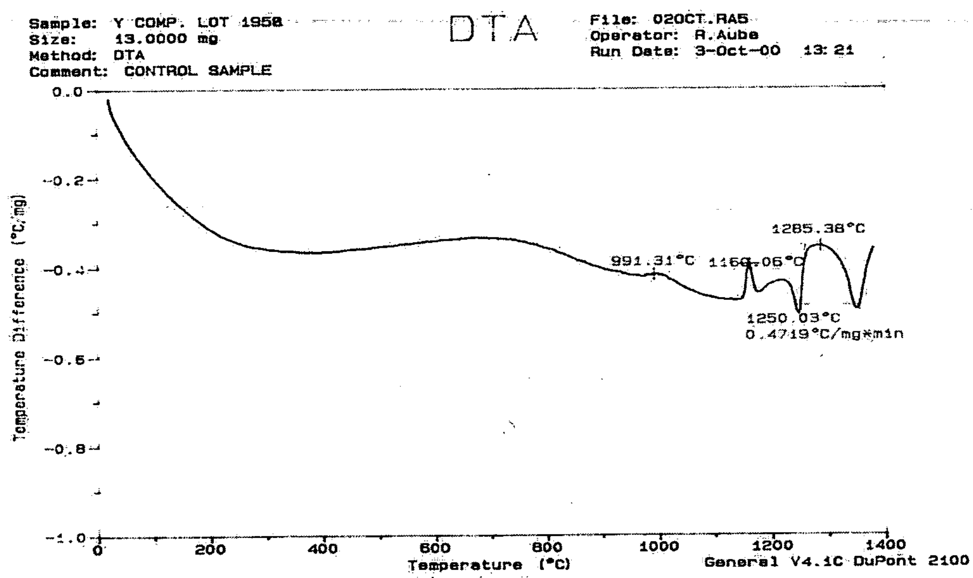
## 4.0 POWDER SENSITIVITY

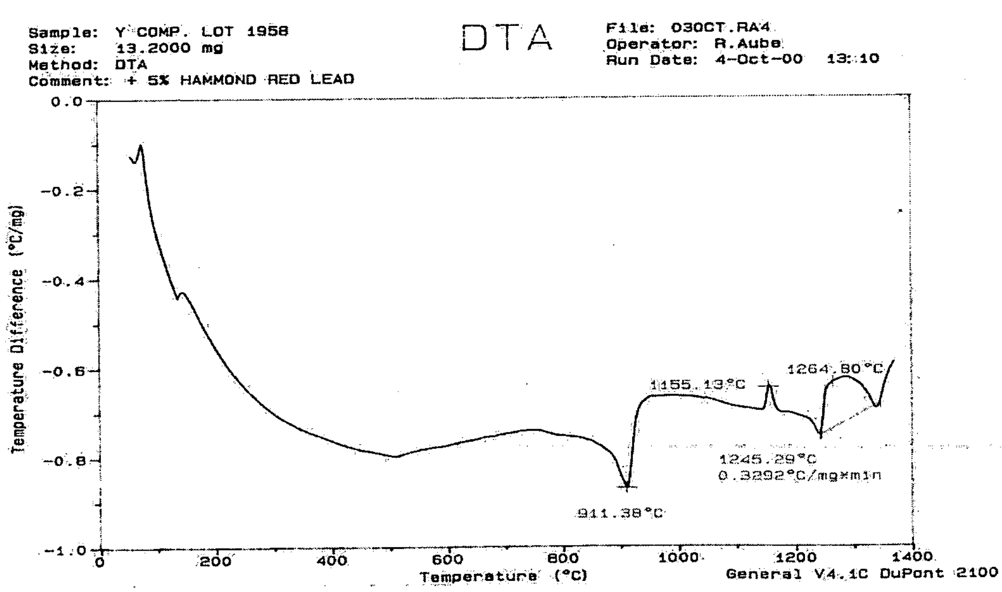
### 4.1 Friction sensitivity

None of the compositions having presence of Red Lead showed signs of ignition when tested for friction sensitivity using the 1.33kg steel torpedo sliding with 30° angle from 30 inch height.

### 4.2 DTA

The DSC charts below shows that the presence of red lead in Y composition reduced its the melting point which facilitated the ignition of the powder.



## 5.0 Methodology of powder loading in zinc element

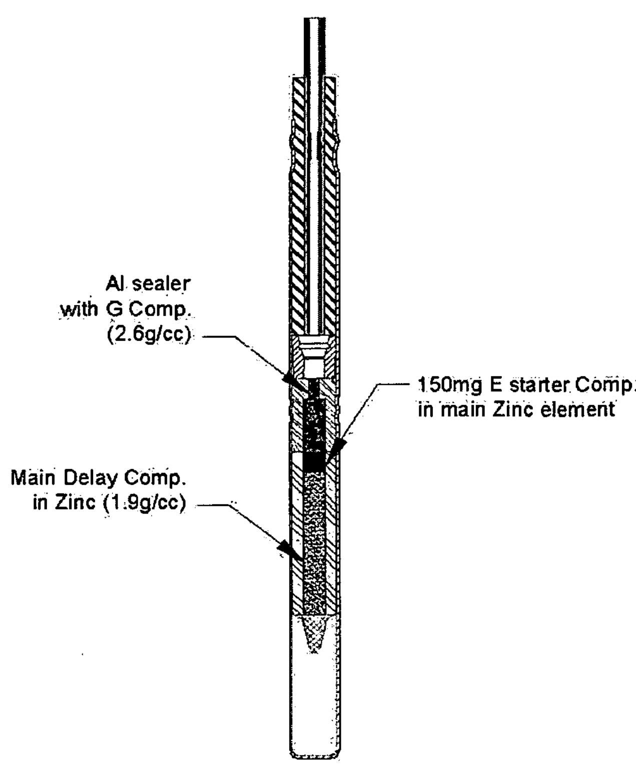
The zinc element is weighed, placed in an holder and the composition is poured into its cavity and pressed at the desired pressure in many small increments until full. The element is weighed again and the powder content recorded. The reliability of powder content in elements was found good for both element length evaluated.

| Element length | charge weight | sample size | SD |
|---|---|---|---|
| 12 mm | 201mg | 30 | 2.1 |
| 30 mm | 504 mg | 30 | 6.0 |

## 6.0 DETONATOR DESIGN

ORICA detonator shell: Although the aluminum rigid sealer type 2 was found very good for timing reliability and stability in the previous evaluation (ETR 1R-86-140), it is not compatible with the ORICA detonator shell design. Frequent instantaneous detonations (4/5) occurred due to the diameter mismatches between element and shell. So, the main zinc element evaluation made using the ORICA detonator shells was done with the regular drawn lead combination of using an E starter + H sealer on top of the main rigid zinc element.

DNES detonator shell: The aluminum rigid sealer type 2 is pressed on top of the main zinc element. Although the DNES detonator design has the primary charge into the main element, the drawing below illustrates the design used for this study.

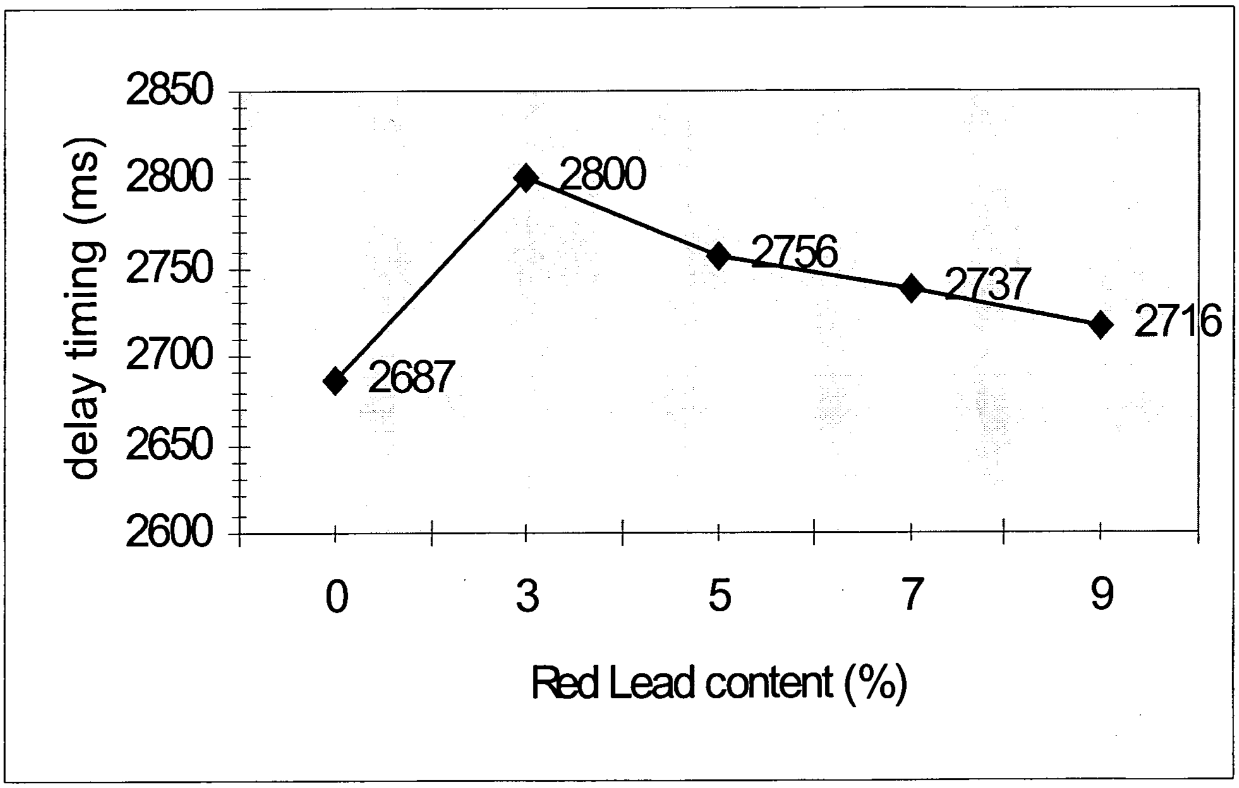


## 7.0 SUMMARY OF TEST RESULTS

### 7.1 Delay timing "vs" Red Lead content in Y comp.

The graph below shows that the presence of Red Lead in composition Y has first, an effect of slowdown the burn rate with the 3% addition of Red Lead and a slight speed increases with the higher Red Lead content.

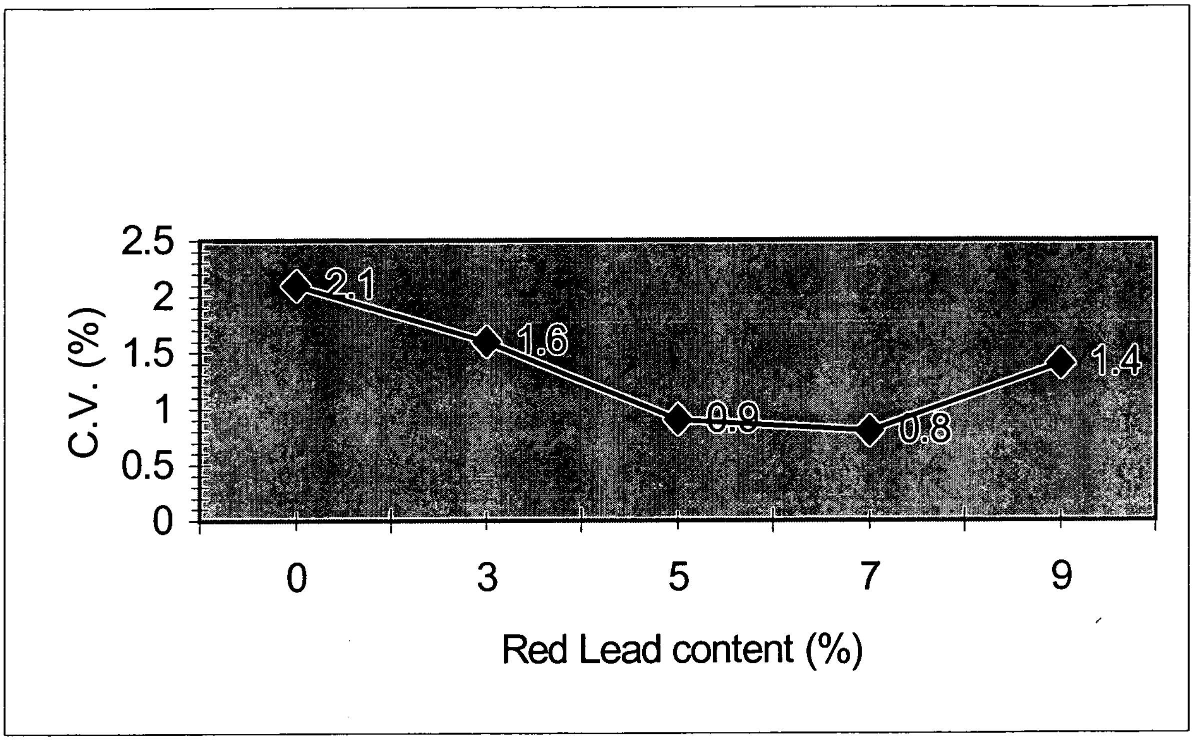
The delay timing were determined in ORICA 2.9 inch detonator shell having a 9.3mm (0.362") zinc element as main and the regular E starter and H sealer from drawn lead tube.



### 7.2 CV's "vs" Red Lead content in Y comp.

From previous timing results, the next graph illustrates the coefficient of variation measured.

It can be seen that any Y comp mix that had the presence of Red Lead in it produced a better timing accuracy than the Y comp control sample.




The sample size for the above results was only 5 detonators per mix, so, in order to confirm the validity of the delay timing obtained, the mix with 5% Red Lead was further loaded in 30 zinc elements and so, in two different element length. They were tested for timing accuracy in ORICA detonator shells and results compared with those obtained by Q.A for this specific lot of composition Y :

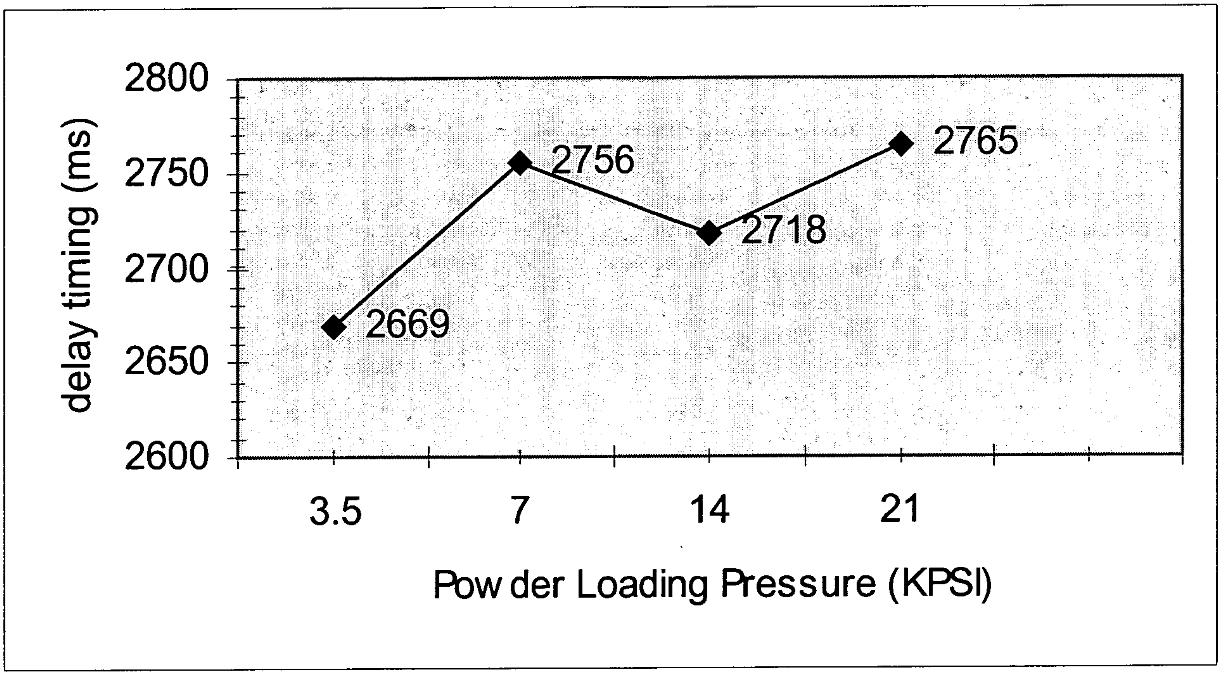
| Zinc element length | Average timing | SD | CV | sample size |
|---|---|---|---|---|
| 12mm | 3487ms | 54 | 1.5 | 30 |
| 30mm | 8383ms | 91 | 1.1 | 30 |

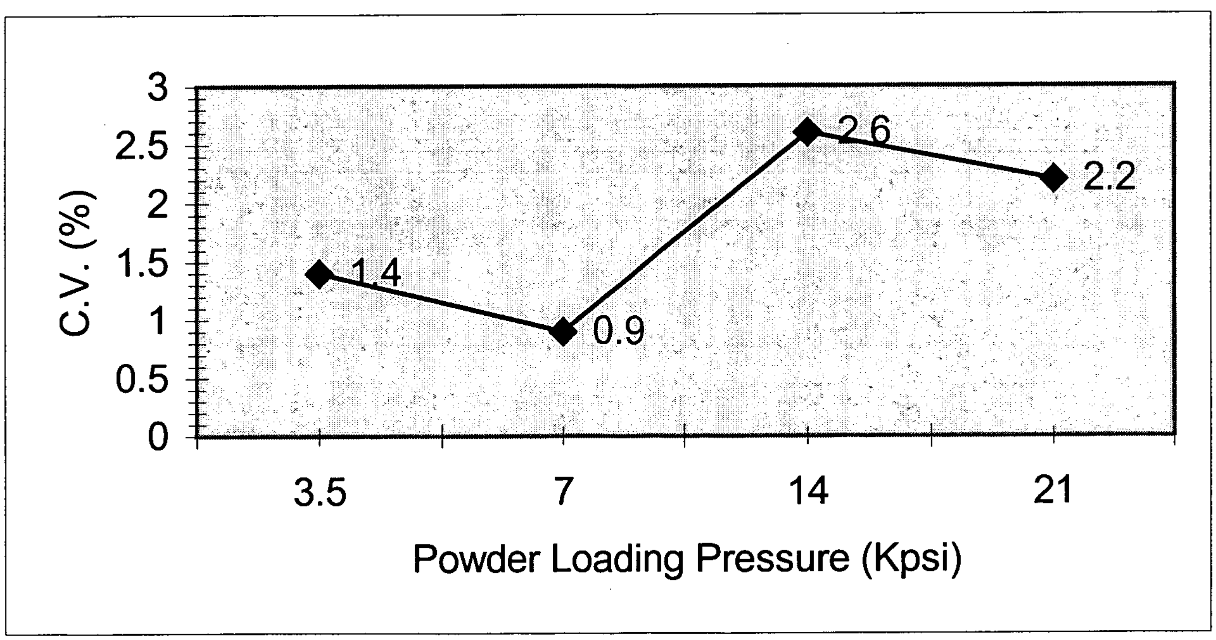
The Q.A. lab (Robin Miller) provided the following timing results for this lot of composition "Y":

1896ms avrg with a SD of 71; cv=3.7% cutting length at 0.305 inch (7.7mm)
9921ms avrg with a SD of 150; cv=1.5% cutting length at 1.318 inch (33.4mm)

### 7.3 Powder loading pressure effect on detonator delay timing

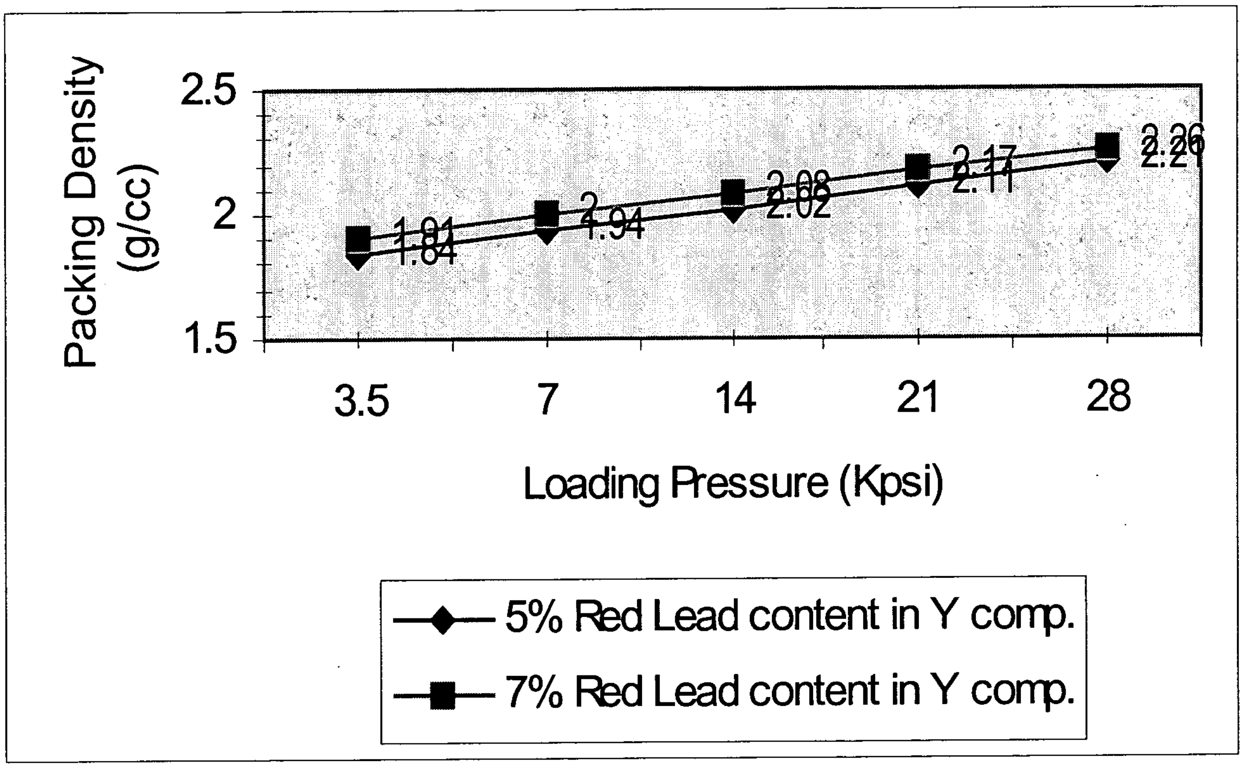
In order to define the proper range for powder loading in rigid zinc elements, the 5% Red Lead content mix was loaded in the 9.30mm elements, pressed at different pressure and fired. Although all detonators made with elements loaded at 28Kpsi failed to ignition, the results illustrated in the graph below indicated that powder loading pressure in the range between 3.5Kpsi to 21Kpsi have a very little effect on the overall timing results. A better timing accuracy is observed for those elements loaded at 3.5Kpsi and 7Kpsi.



### 7.4 Powder density "vs" loading pressure

The density of the delay powder loaded in zinc elements and at different pressure was measured for both mixes having showed the best timing performances. So, according to the previous results, it will be recommended that the powder loading density shall be kept between 1.80 g/cc and 2.00g/cc and more preferably at 1.90g/cc.



### 7.5 Robustness of propagation

The next evaluation was made to measure the timing shift between +20°C and –40°C on various detonator designs in order to demonstrate the advantage of adding some Red Lead in Y composition with either the drawn lead or rigid zinc element technology.

**Note:** **All main elements (lead or zinc) were prepared to be in the same order of delay timing, between 2800ms and 3000ms.**

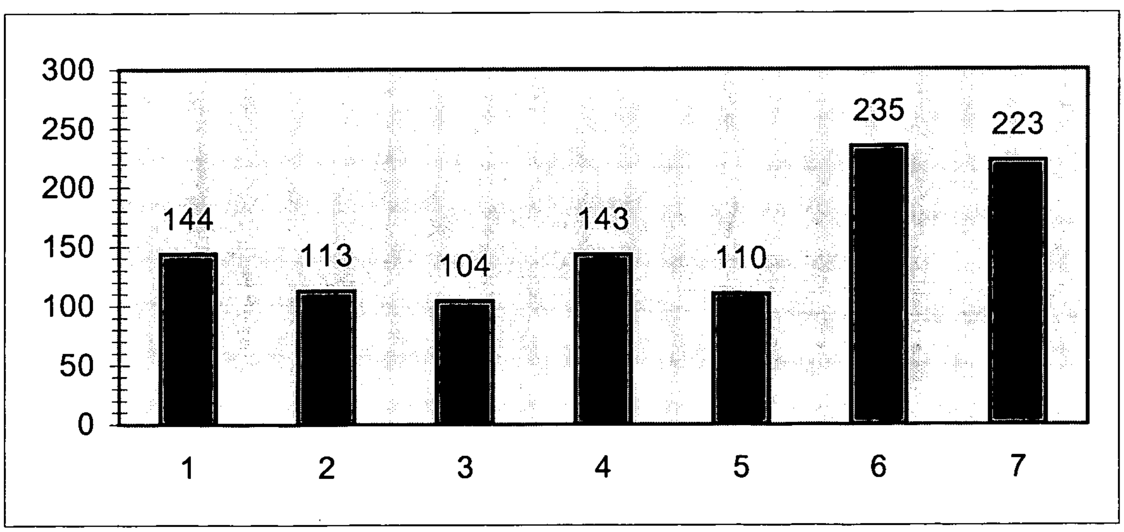
Column 1= Timing shift on Y comp control sample in regular drawn lead & ORICA detonator.
Column 2= Timing shift on Y comp+4% Red Lead in regular drawn lead & ORICA detonator.
Column 3= Timing shift on Y comp+6% Red Lead in regular drawn lead & ORICA detonator.

Column 4= Timing shift on Y comp + 4% Red Lead in zinc main element.
Regular E starter and H sealer from drawn lead in ORICA detonator shell.

Column 5= Timing shift on Y comp + 6% Red Lead in zinc main element.
Regular E starter and H sealer from drawn lead in ORICA detonator shell.

Column 6= Timing shift on Y comp + 6% Red Lead in zinc main element.
150mg of E comp and 100mg of G comp loaded in the aluminum type 2 sealer in DNES detonator shell.

Column 7= Timing shift on Y comp + 6% Red Lead in zinc main element.
150mg of E comp loaded at first in the main element and 215mg of G comp in aluminum type 2 sealer in DNES detonator shell.




Although the ORICA detonator design showed a better timing stability, no failure to ignition was observed on more than 100 detonators fired at –40°C and having a main element made of zinc.

## 7.6 Assessment of the new DNES detonator design .

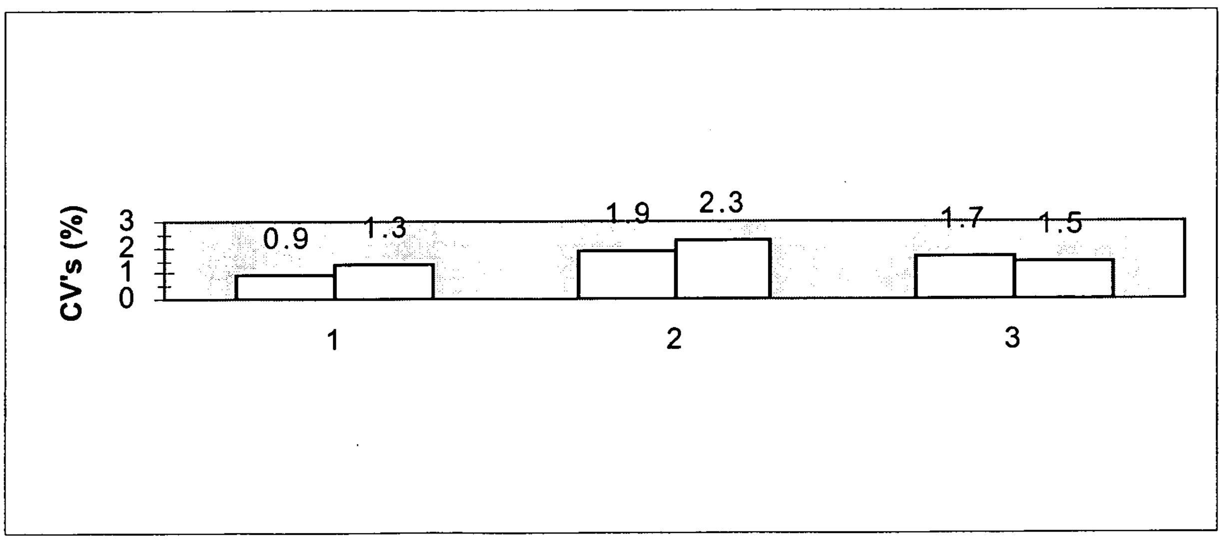
The next and last graph of this report shows the advantage of pressing the E starter composition on top of the delay comp in the main element as opposed to have the E starter comp in the Aluminum sealer with the G composition.

Columns 1= Y comp + 6% Red Lead in 9.30mm zinc main element.
Regular E starter and H sealer from drawn lead in ORICA detonator shell.

Columns 2= Y comp + 6% Red Lead in 9.30mm zinc main element.
150mg of E comp and 150mg of G comp loaded in Aluminum type 2 sealer in DNES detonator shell.

Columns 3= Y comp + 6% Red Lead in 14.0mm zinc main element.
150mg of E comp in main element and 215mg of G comp in Aluminum type 2 sealer in DNES detonator shell.

**Cv's on timing measured at +20°C (column at left) and –40°C (column at right)**




## 8.0 Other detonators evaluation made using Y composition and modified Y compositions in the 30mm zinc elements and, in ORICA detonator design.

| Composition | average timing | SD | CV | sample size |
|---|---|---|---|---|
| AZO 250 $Fe_2O_3$/Si/$Pb_3O_4$ | 4725ms | 236 | 5.0% | 20 (1 det.failure) |
| Harcross 1599D $Fe_2O_3$/Si | 5920ms | --- | --- | 5 (2 det. failure) |
| Y comp as control | 7879ms | --- | --- | 5 (3 det. failure) |
| Y comp + 5% $AL_2O_3$ | 8260ms | 171 | 2.1% | 5 |
| Y comp + 5% $MOO_3$ | 7190ms | 276 | 3.8% | 5 |
| Y comp + 5% Al ATA-105 | 7319ms | 174 | 2.4% | 5 |

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ETR # 1R-86-142

DATE: December 2000.

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# EXPERIMENTAL TEST REPORT

| | | | |
|---|---|---|---|
| **Product:** | DNES detonators | **Instituted by:** | R.F. Stewart |
| **Component:** | Composition Y in zinc elements | **Dept.:** | Technology |
| **Operation:** | Product evaluation | | |
| **Date Started:** | December 2000 | **Date Finished:** | December 2000 |

## SUBJECT

Determine the limits of the new LP composition for the rigid zinc element technology.

## OBJECTIVES

1. Determine the delay timing pattern and accuracy of detonators having a main zinc rigid element filled with the $BaSO_4$/Si system +addition of $Pb_3O_4$.

2. Assess shock resistance of the DNES LP detonators and, of the new LP composition in rigid zinc elements in ORICA detonators.

## CONCLUSION

1. There is a slight delay timing variation for any of those detonators containing between 0% to 12% of Red Lead in Y comp.

2. The DNES LP detonators and the Y comp. mix with 12% Red Lead have showed the best performance against shock pressure.

## RECOMMENDATION

1. Add the binder TYLOSE C-600 in use by DNES for powder processing in zinc elements.

2. Assess detonator performances for wet mixes made with TYLOSE and with 6%, 9% and 12% Red Lead content in the mix.

R. Aubé

Approved by____________

# INDEX

## 1.0 Introduction

The previous ETR 1R-86-140 showed that an addition between 4% to 7% Red Lead in composition Y and loaded in rigid zinc elements at a density between 1.80g/cc to 2.00g/cc produced a very good timing accuracy and functioned reliably at –40°C in either ORICA or DNES detonator shell design.

The present work is an extension of tests where, the maximum quantity of Red Lead that can be added to the composition Y for an Lp detonator was identified and, the resistance to shock stop of such systems was characterized for both, drawn lead and rigid element technology.

## 2.0 Powder mixing

All mixes used for the delay timing evaluation are from small dry mixes where red lead was added in various quantities in Y comp.The ingredients were put together and tumbled in small velostat pots with conductive rubber balls.

The mixes used for the shock resistance evaluation were made wet mix in batch of 700g.

## 3.0 Powder sensitivity
### 3.1 Friction sensitivity

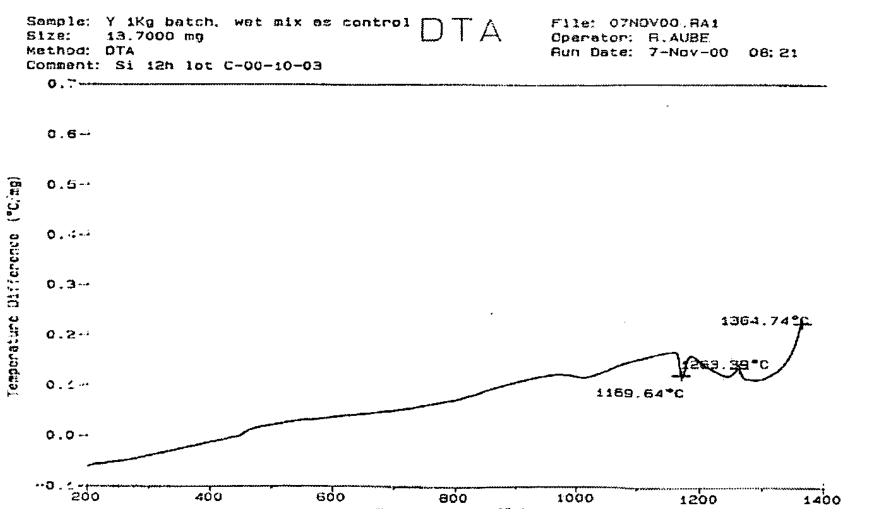
Test description: A steel torpedo of 1.33Kg weight slides on a sample of powder from 30 inch height and 30° angle.

No ignition observed in ten trials when the 12% Red Lead content mix was tested for friction sensitivity.

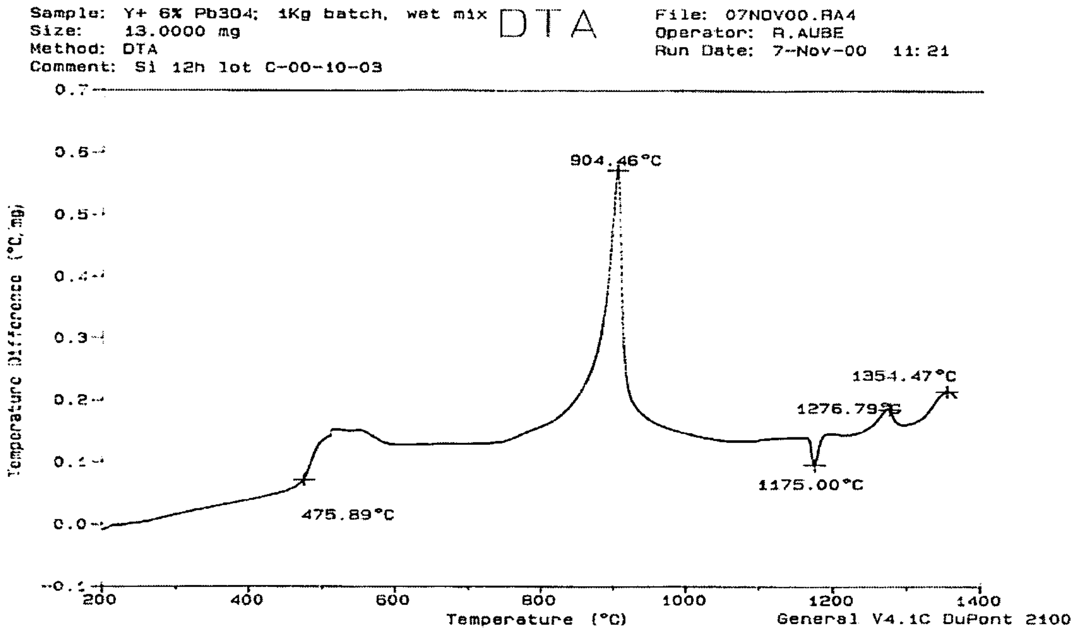
Other powder samples containing less than 9% of Red Lead were also tested for friction sensitivity and did not show any signs of ignition either. Re:ETR 1R-86-140.

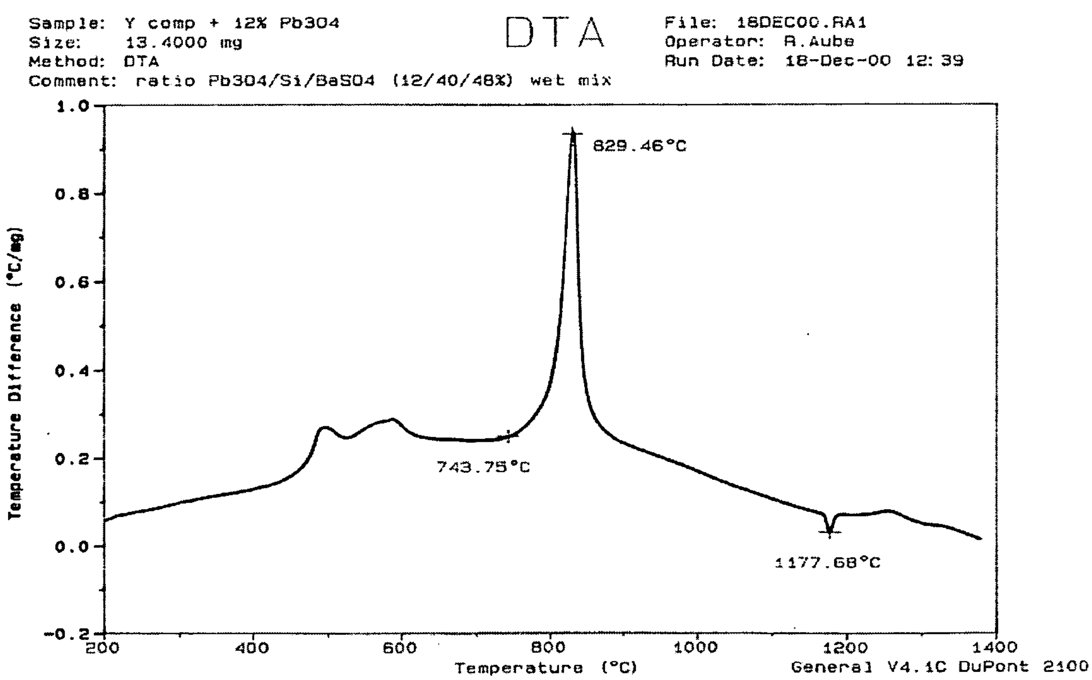
### 3.2 DTA

The DTA analyses were performed on regular Y composition and on modified Y composition that had 6% and 12% of Red Lead in the mix. See following graphs.



The ignition temperature is only shifted by 75°C for those mixes having 6% and 12% Red Lead content in it.



## 4.0 Detonator construction

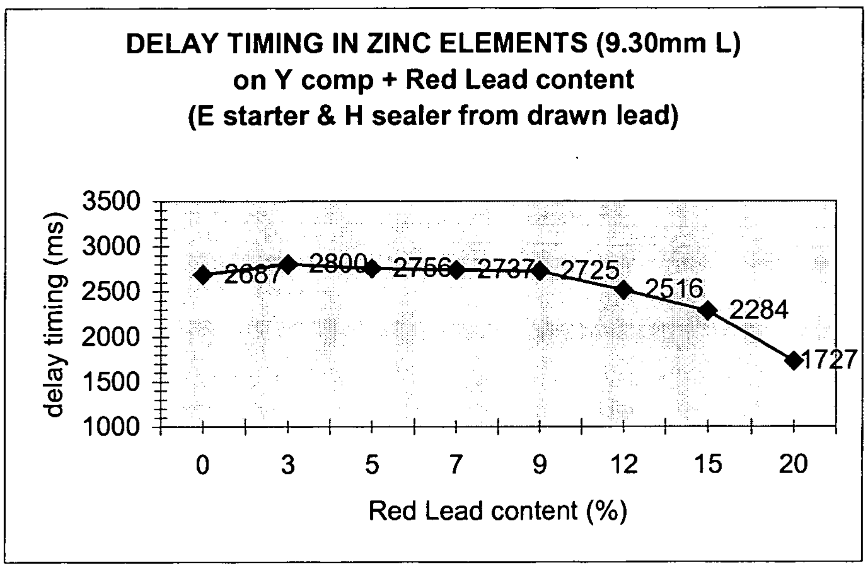
In order to avoid sympathetic detonations during shock stop testing, the Lead Azide charge (110mg) was pressed inside the zinc element cavity. The rest of the cavity was filled with the delay powder. A regular E starter and H sealer was pressed on top of the rigid element and a sealer crimp applied.

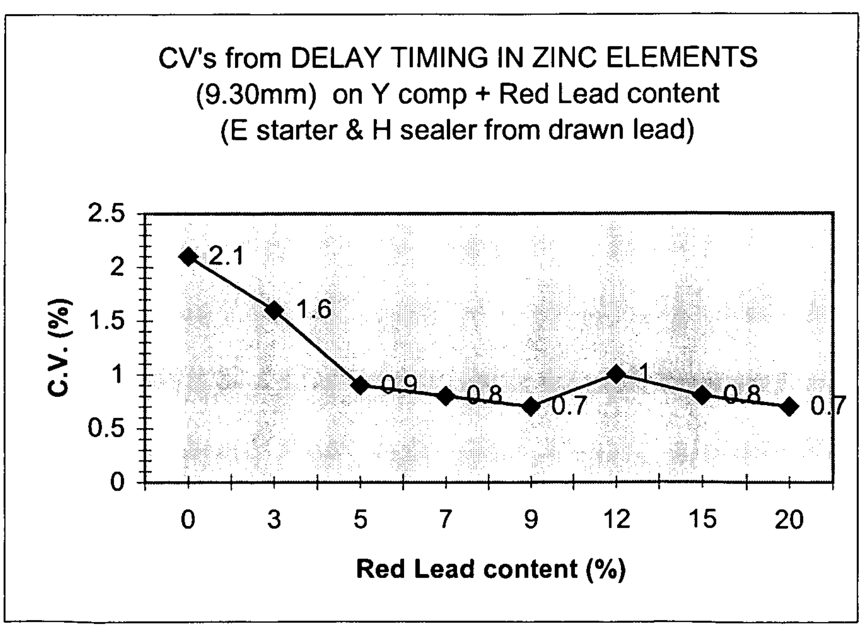
For the same reason expressed above, an LE disc was put on top of the Lead Azide charge for those detonators made with the main delay elements from a drawn lead rod.

## 5.0 Test results

### 5.1 Delay timing

The following graphs show the delay timing pattern for modified Y composition with 0% to 20% Red Lead content. A plateau of relatively stable delay times is observed for those mixes having between 0% and 12 % of red lead added in Y comp.



## 5.2 Shock stop; Test results

The drum test was performed on composition Y and modified comp. Y containing 6% and 12 % of Red Lead .The LP detonators from DNES (7000ms) were also tested for shock resistance.

Test method used: Cooking mode; meaning that both dets are fired simultaneously.

| | | |
|---|---|---|
| Delay timings: | target: | 5000ms and 7000ms |
| | donor: | 2500ms and 3500ms |

The shock pressure test was performed at 14000 Psi (Position #11 in template)

### Test 1 Main delay composition in rigid zinc elements

| | |
|---|---|
| Control sample of Y comp: | 3/10 failures caused by shock stop. |
| Y+ 6% of red lead: | 6/10 failures caused by shock stop. |
| Y+ 12% of red lead: | 0/10 failure |
| DNES 7000ms: | 0/10 failure |

### Test 2 Main delay composition in drawn lead elements

| | |
|---|---|
| Control sample of Y comp: | 5/10 failures caused by shock stop; 1 failed at the LE disc |
| Y+ 6% of red lead: | 8/10 failures caused by shock stop |
| Y+ 12% of red lead: | 6/10 failures caused by shock stop |

**END**